(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 August 2001 (30.08.2001)

PCT

(10) International Publication Number
WO 01/62881 A2

(51) International Patent Classification[7]: C11D

(21) International Application Number: PCT/US01/05530

(22) International Filing Date: 21 February 2001 (21.02.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/184,250 23 February 2000 (23.02.2000) US

(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventor: PRICE, Kenneth, Nathan; 265 Compton Road, Wyoming, OH 45215 (US).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

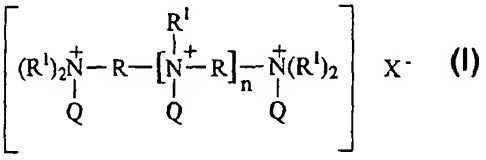
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LAUNDRY DETERGENT COMPOSITIONS COMPRISING HYDROPHOBICALLY MODIFIED POLYAMINES AND NONIONIC SURFACTANTS



(I)

(57) Abstract: The present invention relates to laundry detergent compositions comprising: A) from about 0.01 %, preferably from about 0.1 %, more preferably from about 1 %, most preferably from about 3 % to about 50 %, preferably to about 20 %, more preferably to about 10 %, most preferably to about 7 % by weight, of a hydrophobically modified polyamine having the formula (I) wherein R is C_5-C_{20} linear or branched alkylene, and mixtures thereof; R^1 is an alkyleneoxy unit having the formula: $-(R^2O)_x-R^3$, wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^3 is hydrogen, C_1-C_{22} alkyl, C_7-C_{22} alkylenearyl, an anionic unit, and mixtures thereof; x is from about 15 to about 30; Q is a hydrophobic quaternizing unit selected from the group consisting of C_8-C_{30} linear or branched alkyl, C_6-C_{30} cycloalkyl, C_7-C_{30} substituted or unsubstituted alkylenearyl, and mixtures thereof; X is an anion present in sufficient amount to provide electronic neutrality; n is from 0 to 4; B) from about 0.01 % by weight, of a surfactant system comprising one or more surfactants selected from: i) from about 85 % to about 99.9 % by weight, of one or more nonionic surfactants; ii) optionally, from about 0.1 % to about 15 % by weight, of one or more anionic surfactants; iii) optionally from about 0.1 % to about 15 % by weight, of one or more cationic surfactants; iv) optionally from about 0.1 % to about 15 % by weight, of one or more zwitterionic surfactants; v) optionally from about 0.1 % to about 15 % by weight, of one or more ampholytic surfactants; or vi) mixtures thereof; C) the balance carriers and adjunct ingredients.

WO 01/62881 A2

LAUNDRY DETERGENT COMPOSITIONS COMPRISING HYDROPHOBICALLY MODIFIED POLYAMINES AND NONIONIC SURFACTANTS

CROSS-REFERENCE

This Application claims the benefit of U.S. Provisional Application no. 60/184,250, filed on February 23, 2000.

FIELD OF THE INVENTION

The present invention relates to laundry detergent compositions comprising one or more hydrophobically modified polyamines and nonionic surfactants which provide enhanced hydrophilic soil, *inter alia*, clay, removal benefits. The present invention also relates to methods for removing hydrophilic soil form wearing apparel.

BACKGROUND OF THE INVENTION

Fabric, especially clothing, can become soiled with a variety of foreign substances ranging from hydrophobic stains (grease, oil) to hydrophilic stains (clay). The level of cleaning which is necessary to remove said foreign substances depends to a large degree upon the amount of stain present and the degree to which the foreign substance has contacted the fabric fibers. Grass stains usually involve direct abrasive contact with vegetative matter thereby producing highly penetrating stains. Clay soil stains, although in some instances contacting the fabric fibers with less force, nevertheless provide a different type of soil removal problem due to the high degree of charge associated with the clay itself. This high surface charge density may act to repel some laundry adjunct ingredients, *inter alia*, clay dispersants, thereby resisting any appreciable peptization and dispersal of the clay into the laundry liquor.

A surfactant per se is not all that is necessary to remove unwanted clay soils and stains. In fact, most surfactants by themselves in water are surprisingly poor at removing clay soils from fabric. not all surfactants work equally well on all types of stains. In addition to surfactants, polyamine-based hydrophilic soil dispersants are added to laundry detergent compositions to "carry away" clay soils from the fabric surface and to stabilize the removed particles in solution sufficiently to minimize the possibility that the clay soil will be re-deposited upon the fabric.

However, unless the clay can be initially removed from the soiled fabric, especially in the case of hydrophilic fibers, *inter alia*, cotton, there will be nothing in solution for the dispersants to bind to and keep suspended.

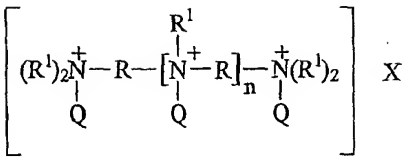
There is a long felt need in the art for laundry detergent compositions which can effectively break up and remove embedded clay and other hydrophilic soils from fabric. In addition, as the concentration of hydrophilic soil increases in the laundry liquor, there is a need for a surfactant system which will be able to handle this increased soil load. Also there is a long felt need for a clay soil active adjunct ingredient which can be optimized to fit the particular laundry detergent embodiment, *inter alia*, granular, liquid, and which can be therefore tailored to match the surfactant system. There has further been a long felt need for a method for cleaning hydrophilic soils from fabric wherein the hydrophilic soils are effectively peptized, dispersed, and suspended in the laundry liquor.

SUMMARY OF THE INVENTION

It has now been surprisingly discovered that laundry detergent compositions comprising fully quaternized polyethoxylated polyamines wherein said polyethoxy units are capped with anionic units and wherein the polyamine backbone is comprised of relatively hydrophobic backbone spacer units, said polyamines can be hydrophobically modified by the selection of certain quaternizing units to provide enhanced removal of soils from clothing. The laundry detergent compositions of the present invention are especially effective in removal of clay and other hydrophilic soils from fabric. When used together with a suitable surfactant system, the hydrophobically modified polyamines of the present invention provides for removal of stains which were once believed ruinous to fabric, especially cellulose comprising fabric.

The first aspect of the present invention relates to laundry detergent compositions comprising:

A) from about 0.01%, preferably from about 0.1%, more preferably from about 1%, most preferably from about 3% to about 50%, preferably to about 20%, more preferably to about 10%, most preferably to about 7% by weight, of a hydrophobically modified polyamine having the formula:



wherein R is C_5-C_{20} linear or branched alkylene, and mixtures thereof; R^1 is an alkyleneoxy unit having the formula:

$$-(R^2O)_x-R^3$$

wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^3 an anionic unit, and mixtures thereof; x is from about 15 to about 30; Q is a hydrophobic quaternizing unit selected from the group consisting of C_8-C_{30} linear or branched alkyl, C_6-C_{30} cycloalkyl, C_7-C_{30} substituted or unsubstituted alkylenearyl, and mixtures thereof; X is an anion present in sufficient amount to provide electronic neutrality; n is from 0 to 4;

B) from about 0.01% by weight, of a surfactant system comprising one or more nonionic surfactants; and

C) the balance carriers and adjunct ingredients.

The present invention further relates to a zwitterionic polyamine in combination with a high nonionic surfactant detersive surfactant system. The high nonionic surfactant systems of the present invention comprise:

i) from about 85% to about 99.9% by weight, of one or more nonionic surfactants;

ii) optionally, from about 0.1% to about 15% by weight, of one or more anionic surfactants;

iii) optionally from about 0.1% to about 15% by weight, of one or more cationic surfactants;

iv) optionally from about 0.1% to about 15% by weight, of one or more zwitterionic surfactants;

v) optionally from about 0.1% to about 15% by weight, of one or more ampholytic surfactants; or

vi) mixtures thereof.

The present invention also relates to a method for cleaning fabric, said method comprising the step of contacting an article of manufacture comprising fabric, preferably clothing, with an

aqueous solution of a laundry detergent composition comprising a hydrophobically modified polyamine and a high nonionic surfactant system of the present invention.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (° C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to hydrophobically modified quaternized zwitterionic polyamines which are suitable for use in laundry detergent compositions which comprise only nonionic surfactants or which comprise a surfactant system which is high in nonionic surfactants. The hydrophobically modified zwitterionic polyamines of the present invention provide enhanced body soil and perspiration soil removal benefits.

It has been surprisingly discovered that hydrophobically modified quaternized zwitterionic polyamines in combination with high levels of nonionic surfactants have increased effectiveness when treating fabric which is soiled with human body oils, perspiration, etc. Without wishing to be limited by theory, the hydrophobically modified quaternary zwitterionic polyamines of the present invention have an unexpected balance of properties which makes the compounds amenable to penetrating fabric to solublize greasy, oily stains, while maintaining water solubility, and preserving the particulate soil suspension properties needed to direct the dirt away from the fabric thereby avoiding re-deposition. In addition, the hydrophobically modified zwitterionic polyamines of the present invention reinforce the cleaning actions of high nonionic surfactant comprising cleaning systems.

For the purposes of the present invention the term "high level of nonionic surfactant" is defined as "a surfactant system comprising from about 85%, preferably from about 90%, more preferably from about 95% by weight to about 99.9% by weight, of one or more nonionic surfactants" as described herein below.

When present in laundry detergent compositions, the zwitterionic polyamines are effective in an amount from about 0.01%, preferably from about 0.1%, more preferably from about 1%, most preferably from about 3% to about 50%, preferably to about 20%, more preferably to about 10%, most preferably to about 7% by weight, of said laundry detergent composition.

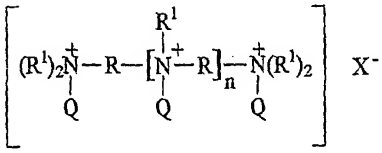
The following is a detailed description of the required elements of the present invention.

Hydrophobically Modified Quaternized Zwitterionic Polyamines

For the purposes of the present invention the term "hydrophobically modified" is defined herein as the "reaction of a linear polyamine comprising from 2 to 5 nitrogens wherein each nitrogen has its backbone hydrogens replaced by an anionic unit-capped polyalkyleneoxy unit comprising at least about 15 alkyleneoxy units, with at least one equivalent per nitrogen of a quaternizing agent, said quaternizing agents comprising a linear alkyl moiety having at least 8 carbon atoms, a cyclic alkyl moiety having at least 6 carbon atoms, an alkylenearyl unit, *inter alia*, benzyl, having at least 7 carbon atoms, or mixtures thereof".

A "polyamine" for the purposes of the present invention is "an amine having less than 6 backbone nitrogen atoms and no branching", whereas for the purposes of the present invention, amines comprising more than 5 nitrogens are defined as "oligomeric amines" (oligoamines) or "polymeric amines" (polyalkyleneamines or polyalkyleneimines).

The hydrophobically modified zwitterionic polyamines of the present invention have the formula:



wherein R is C_6-C_{20} linear or branched alkylene, and mixtures thereof; preferably C_6-C_{10} linear alkylene, more preferably C_6-C_8 linear alkylene, most preferred backbone unit R is hexylene.

R^1 is an alkyleneoxy unit having the formula:

$$-(R^2O)_x-R^3$$

wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof. Preferably R^2 comprises ethylene, 1,2-propylene, and mixtures thereof, preferably each R^2 unit is an ethylene unit. One embodiment of the present invention which provides advantages in a bleach comprising composition relates to hydrophobically modified zwitterionic polyamines comprising the first 1-6, preferably the first 1-3 of alkyleneoxy units as 1,2-propyleneoxy units followed by the balance ethyleneoxy units.

R^3 is an anionic unit, and mixtures thereof. Non-limiting examples of preferred anionic units according to the present invention are selected from

a) $-(CH_2)_tCO_2M$;

b) $-C(O)(CH_2)_fCO_2M$;

c) $-(CH_2)_fPO_3M$;

d) $-(CH_2)_fOPO_3M$;

e) $-(CH_2)_fSO_3M$;

f) $-CH_2(CHSO_3M)(CH_2)_fSO_3M$;

g) $-CH_2(CHSO_2M)(CH_2)_fSO_3M$;

h) $-C(O)CH_2CH(SO_3M)CO_2M$;

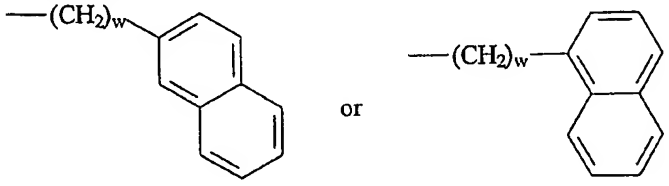
i) $-C(O)CH_2CH(CO_2M)NHCH(CO_2M)CH_2CO_2M$;

j) and mixtures thereof;

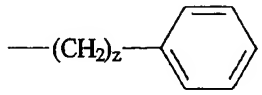
wherein M is hydrogen or a cation which provides charge neutrality. For the purposes of the present invention, all M units, whether associated with a hydrophobically modified zwitterionic polyamine, surfactant, or adjunct ingredient, can either be a hydrogen atom or a cation depending upon the form isolated by the artisan or the relative pH of the system wherein the compound is used. Non-limiting examples of preferred cations include sodium, potassium, ammonium, and mixtures thereof. The index f is from 0 to about 10, preferably from 0 to 2.

The index x which describes the average number of alkyleneoxy units attached to the backbone nitrogen is from about 15 to about 30,preferably from 15 to 25, more preferably from 18 to 23, most preferred average value of alkyleneoxy units is 20. The formulator will recognize that when ethoxylating a zwitterionic polyamine, only an average number or statistical distribution of alkyleneoxy units will be know. Therefore, depending upon how "tightly" or how "exactly" a zwitterionic polyamine is alkoxylated, the average value may vary from embodiment to embodiment.

Each Q is independently C_8-C_{30} linear or branched alkyl, C_6-C_{30} cycloalkyl, C_7-C_{30} substituted or unsubstituted alkylenearyl, and mixtures thereof; preferably Q is a hydrophobic quaternizing unit selected from the group consisting of C_7-C_{30} substituted or unsubstituted alkylenearyl, and mixtures thereof; more preferably benzyl, substituted benzyl, naphthyl, substituted naphthyl, and mixtures thereof. For the purposes of the present invention the formulae:



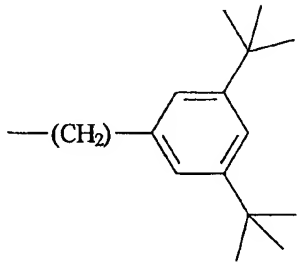
stands for the term "naphthyl" depending upon whether said unit comprises α-substitution or β-substitution. The index w has the value from 0 to 20. Other alkylene aryl units include besides benzyl, alkylenearyl units having the formula:



wherein the index z is from 1 to 24.

For the purposes of the present invention the term "substituted" as it applies to alkylenearyl units suitable as Q units, are one or more C_1-C_{12} linear or branch alkyl moieties, provided the total number of carbon atoms including the aromatic ring does not exceed 30 carbon atoms.

A non-limiting example of a substitued alkylenearyl unit according to the present invention has the formula:

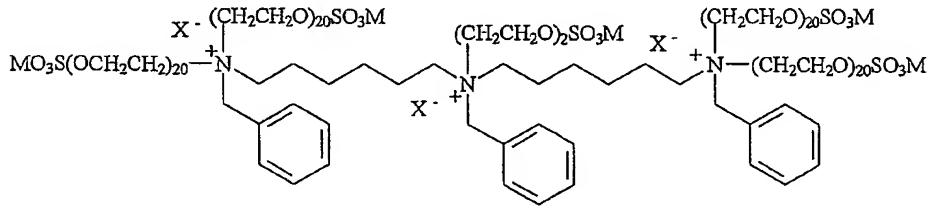


which is a 3,5-di-tert-butyl benzyl moiety.

The index n represents the number of secondary nitrogens in the backbone. The index n has the value from 0 to 4, preferably from 0 to 2.

X is an anion present in sufficient amount to provide electronic neutrality. Non- limiting examples of anions are chlorine, bromine, iodine, methylsulfate, and mixtures thereof.

An example of a preferred hydrophobically modified zwitterionic polyamine according to the present invention has the formula:



wherein X is a water soluble anion selected from the group consisting of chlorine, bromine, iodine, methylsulfate, and mixtures thereof.

SURFACTANT SYSTEM

The laundry detergent compositions of the present invention comprise from about 0.01%, preferably from about 1%, more preferably from about 5%, most preferably from 10% to about 80%, preferably to about 50%, more preferably to about 30% by weight, of a surfactant system, said surfactant system comprising one or more nonionic surfactants.

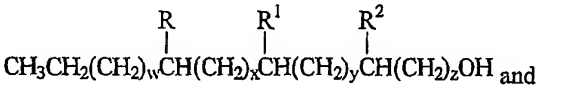
Non-limiting examples of nonionic surfactants according to the present invention include:

i) C_{12}-C_{18} alkyl ethoxylates, *inter alia*, NEODOL® nonionic surfactants ex Shell;

ii) C_6-C_{12} alkyl phenol alkoxylates wherein the alkoxylate units are a mixture of ethyleneoxy and propyleneoxy units;

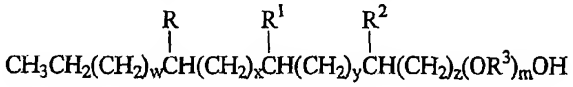
iii) C_{12}-C_{18} alcohol and C_6-C_{12} alkyl phenol condensates with ethylene oxide/propylene oxide block polymers *inter alia* Pluronic® ex BASF which are disclosed in U.S. 3,929,678 Laughlin et al., issued December 30, 1975, incorporated herein by reference;

iv) C_{14}-C_{22} mid-chain branched alcohols, BA having the formula:



and

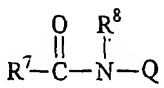
v) C_{14}-C_{22} mid-chain branched alkyl alkoxylates, BAE_x having the formula:



wherein R, R^1, and R^2 are each independently hydrogen, C_1-C_3 alkyl, and mixtures thereof; provided at least one of R, R^1, and R^2 is not hydrogen; preferably R, R^1, and R^2 are methyl; preferably one of R, R^1, and R^2 is methyl and the other units are hydrogen. The total number of carbon atoms in the mid-chain branched alkyl sulfate and alkyl alkoxy sulfate surfactants is from 14 to 20; the index w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; provided w + x + y + z is from 8 to 14 and the total number of carbon atoms in a surfactant is from 14 to 20; R^3 is C_1-C_4 linear or branched alkylene, preferably ethylene, 1,2-propylene, 1,3-propylene, 1,2-butylene, 1,4-butylene, and mixtures thereof;

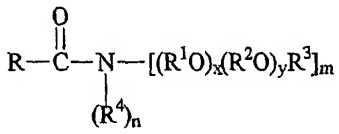
vi) Alkylpolysaccharides as disclosed in U.S. 4,565,647 Llenado, issued January 26, 1986, incorporated herein by reference;

vii) Polyhydroxy fatty acid amides having the formula:



wherein R^7 is C_5-C_{31} alkyl; R^8 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, Q is a polyhydroxyalkyl moiety having a linear alkyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof; preferred alkoxy is ethoxy or propoxy, and mixtures thereof; preferred Q is derived from a reducing sugar in a reductive amination reaction, more preferably Q is a glycityl moiety; Q is more preferably selected from the group consisting of $-CH_2(CHOH)_nCH_2OH$, $-CH(CH_2OH)(CHOH)_{n-1}CH_2OH$, $-CH_2(CHOH)_2(CHOR')(CHOH)\ CH_2\ OH$, and alkoxylated derivatives thereof, wherein n is an integer from 3 to 5, inclusive, and R' is hydrogen or a cyclic or aliphatic monosaccharide, which are described in U.S. 5,489,393 Connor et al., issued February 6, 1996; and U.S. 5,45,982 Murch et al., issued October 3, 1995, both incorporated herein by reference.

A non-limiting example of a nonionic surfactant suitable for use in the present invention has the formula:



wherein R is C_7-C_{21} linear alkyl, C_7-C_{21} branched alkyl, C_7-C_{21} linear alkenyl, C_7-C_{21} branched alkenyl, and mixtures thereof.

R^1 is ethylene; $R^2$is C_3-C_4 linear alkyl, C_3-C_4 branched alkyl, and mixtures thereof; preferably R^2 is 1,2-propylene. Nonionic surfactants which comprise a mixture of R^1 and R^2units preferably comprise from about 4 to about 12 ethylene units in combination with from about 1 to about 4 1,2-propylene units. The units may be alternating, or grouped together in any combination suitable to the formulator. Preferably the ratio of R^1 units to R^2 units is from about 4 : 1 to about 8 : 1. Preferably an R^2 units (i.e. 1,2-propylene) is attached to the nitrogen atom followed by the balance of the chain comprising from 4 to 8 ethylene units.

R^2 is hydrogen, C_1-C_4 linear alkyl, C_3-C_4 branched alkyl, and mixtures thereof; preferably hydrogen or methyl, more preferably hydrogen.

R^4 is hydrogen, C_1-C_4 linear alkyl, C_3-C_4 branched alkyl, and mixtures thereof; preferably hydrogen. When the index m is equal to 2 the index n must be equal to 0 and the R^4 unit is absent and is instead replaced by a $-[(R^1O)_x(R^2O)_yR^3]$ unit.

The index m is 1 or 2, the index n is 0 or 1, provided that when m is equal to 1, n is equal to 1; and when m is 2 n is 0; preferably m is equal to 1 and n is equal to one, resulting in one -$[(R^1O)_x(R^2O)_yR^3]$ unit and R^4 being present on the nitrogen. The index x is from 0 to about 50, preferably from about 3 to about 25, more preferably from about 3 to about 10. The index y is from 0 to about 10, preferably 0, however when the index y is not equal to 0, y is from 1 to about 4. Preferably all of the alkyleneoxy units are ethyleneoxy units. Those skilled in the art of ethoxylated polyoxyalkylene alkyl amide surface active agents will recognized that the values for the indices x and y are average values and the true values may range over several values depending upon the process used to alkoxylate the amides.

The compositions of the present invention may also comprise high nonionic surfactant comprising surfactant systems. The systems of the present invention comprise:

i) from about 85% to about 99.9% by weight, of one or more nonionic surfactants;

ii) optionally, from about 0.1% to about 15% by weight, of one or more anionic surfactants;

iii) optionally from about 0.1% to about 15% by weight, of one or more cationic surfactants;

iv) optionally from about 0.1% to about 15% by weight, of one or more zwitterionic surfactants;

v) optionally from about 0.1% to about 15% by weight, of one or more ampholytic surfactants; or

vi) mixtures thereof.

Non-limiting examples of surfactants other than nonionic surfactants which are suitable for use in the present invention include:

a) C_{11}-C_{18} alkyl benzene sulfonates (LAS);

b) C_6-C_{18} mid-chain branched aryl sulfonates (BLAS);

c) C_{10}-C_{20} primary, α or ω-branched, and random alkyl sulfates (AS);

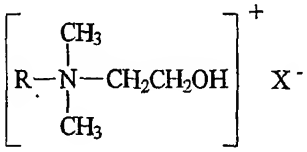
d) C_{14}-C_{20} mid-chain branched alkyl sulfates (BAS);

e) C_{10}-C_{18} secondary (2,3) alkyl sulfates as described in U.S. 3,234,258 Morris, issued February 8, 1966; U.S. 5,075,041 Lutz, issued December 24, 1991; U.S. 5,349,101 Lutz et al., issued September 20, 1994; and U.S. 5,389,277 Prieto, issued February 14, 1995 each incorporated herein by reference;

f) C_{10}-C_{18} alkyl alkoxy sulfates (AE_xS) wherein preferably x is from 1-7;

g) C_{14}-C_{20} mid-chain branched alkyl alkoxy sulfates (BAE_xS).

An example of a preferred cationic surfactant according to the present invention includes cationic surfactants having the formula:



wherein R is C_{12}-C_{14} alkyl and X is a water soluble cation.

FORMULATIONS

The compositions of the present invention may be in any form, *inter alia*, liquid, granular, paste. Depending upon the specific form of the laundry composition, as well as, the expected use thereof, the formulator may will use different surfactant and adjunct ingredient combinations.

Preferably the Heavy Duty Granular compositions according to the present invention comprise:

a) from about 0.01%, preferably from about 0.1%, more preferably from 1%, most preferably from 3% to about 20%, preferably to about 10%, more preferably to about 7% by weight, of a hydrophobically modified polyamine; and

b) from about 0.01%, preferably from about 1%, more preferably from about 5%, most preferably from 10% to about 80%, preferably to about 50%, more preferably to about 30% by weight of a surfactant system, said surfactant system comprising:

i) from about 85%, preferably from about 90%, more preferably from about 95% by weight to about 99.9% by weight, of the surfactant system one or more nonionic surfactants;

ii) optionally and preferably, from 0.1%, preferably from about 5% more preferably from about 10% to about 15% by weight, of the surfactant system of one or more anionic surfactants;

iii) optionally and preferably, from 0.1%, preferably from about 5% more preferably from about 10% to about 15% by weight, of one or more zwitterionic, cationic, ampholytic surfactants, and mixtures thereof.

HDG laundry detergent compositions will typically comprise more of anionic detersive surfactants than nonionic surfactants, however, in one preferred embodiment of the present invention relating to detergents in the form of a bar wherein surfactants are used as binders as well as functioning as detersive agents, at least about 50% by weight, of the HDG surfactant systems will comprise nonionic surfactants.

BLEACHING SYSTEM

The hydrophobically modified polyamine, nonionic surfactant system comprising laundry detergent compositions of the present invention may optionally comprise a bleaching system. Bleaching systems typically comprise a "bleaching agent" (source of hydrogen peroxide) and an "initiator" or "catalyst".

Preferred laundry detergent compositions of the present invention which comprise a bleaching system, comprise:

a) from about 0.01% by weight, of a hydrophobically modified polyamine according to the present invention;

b) from about 0.01% by weight, of a surfactant system comprising:

   i) from 0% to 100% by weight, of the surfactant system one or more anionic surfactants;

   ii) from 0% to 100% by weight, of the surfactant system one or more nonionic surfactants;

   iii) optionally from 0.1% to about 80% by weight, of the surfactant system one or more cationic surfactants;

   iv) optionally from 0.1% to about 80% by weight, of the surfactant system one or more zwitterionic surfactants;

   v) optionally from 0.1% to about 80% by weight, of the surfactant system one or more ampholytic surfactants; or

   vi) mixtures thereof;

c) from about 1%, preferably from about 5% to about 80%, preferably to about 50% by weight, of the laundry detergent composition, a peroxygen bleaching system comprising:

i) from about 40%, preferably from about 50%, more preferably from about 60% to about 100%, preferably to about 95%, more preferably to about 80% by weight, of the bleaching system, a source of hydrogen peroxide;

ii) optionally from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the beaching system, a beach activator;

iii) optionally from about 1 ppb (0.0000001%), more preferably from about 100 ppb (0.00001%), yet more preferably from about 500 ppb (0.00005%), still more preferably from about 1 ppm (0.0001%) to about 99.9%, more preferably to about 50%, yet more preferably to about 5%, still more preferably to about 500 ppm (0.05%) by weight of the composition, of a transition-metal bleach catalyst;

iv) optionally from about 0.1% by weight, of a pre-formed peroxygen bleaching agent; and

d) the balance carriers and other adjunct ingredients.

Bleaching Agents - Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

Sources of hydrogen peroxide which are suitable for use in the compositions of the present invention include, but are not limited to, perborates, percarbonates, perphosphates, persulfates, and mixtures thereof. Preferred sources of hydrogen peroxide are sodium perborate monohydrate, sodium perborate tetrahydrate, sodium percarbonate and sodium persulfate, more preferably are sodium perborate monohydrate, sodium perborate tetrahydrate, and sodium percarbonate. When present the source of hydrogen peroxide is present at a level of from about 40%, preferably from about 50%, more preferably from about 60% to about 100%, preferably to about 95%, more preferably to about 80% by weight, of the bleaching system. Embodiments which are bleach comprising pre-soak compositions may comprise from 5% to 99% of the source of hydrogen peroxide.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by

weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants.

Bleach Activators

Preferably, the source of hydrogen peroxide (peroxygen bleach component) in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01%, preferably from about 0.5%, more preferably from about 1% to about 15%, preferably to about 10%, more preferably to about 8%, by weight of the composition. Also, bleach activators will comprise from about 0.1% to about 60% by weight, of the beaching system. When the herein described bleaching system comprises 60% by weight, of an activator (the maximal amount) and said composition (bleaching composition, laundry detergent, or otherwise) comprises 15% by weight of said activator (the maximal amount by weight), said composition will comprise 25% by weight of a bleaching system (60% of which is bleach activator, 40% a source of hydrogen peroxide). However, this is not meant to restrict the formulator to a 60:40 ratio of activator to hydrogen peroxide source.

Preferably the mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1, more preferably from about 10:1 to about 1:1, preferably to about 3:1.

Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C_{10}-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred hydrophobic bleach activators include, but are not limited to, nonanoyloxybenzenesulphonate (NOBS), 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) an example of which is described in U.S. Patent No. 5,523,434, dodecanoyloxybenzenesulphonate (LOBS or C_{12} -OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C_{11}-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

Preferred bleach activators are those described in U.S. 5,698,504 Christie et al., issued December 16, 1997; U.S. 5,695,679 Christie et al. issued December 9, 1997; U.S. 5,686,401 Willey et al., issued November 11, 1997; U.S. 5,686,014 Hartshorn et al., issued November 11,

1997; U.S. 5,405,412 Willey et al., issued April 11, 1995; U.S. 5,405,413 Willey et al., issued April 11, 1995; U.S. 5,130,045 Mitchel et al., issued July 14, 1992; and U.S. 4,412,934 Chung et al., issued November 1, 1983, and copending patent applications U. S. Serial Nos. 08/709,072, 08/064,564; acyl lactam activators, as described in U.S. 5,698,504, U.S. 5,695,679 and U.S. 5,686,014, each of which is cited herein above, are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams, U.S. 5,503,639 Willey et al., issued April 2, 1996 all of which are incorporated herein by reference.

Quaternary substituted bleach activators may also be included. The present cleaning compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. 5,686,015 Willey et al., issued November 11, 1997; U.S. 5,654,421 Taylor et al., issued August 5, 1997; U.S. 5,460,747 Gosselink et al., issued October 24, 1995; U.S. 5,584,888 Miracle et al., issued December 17, 1996; and U.S. 5,578,136 Taylor et al., issued November 26, 1996; all of which are incorporated herein by reference.

Highly preferred bleach activators useful herein are amide-substituted as described in U.S. 5,698,504, U.S. 5,695,679, and U.S. 5,686,014 each of which are cited herein above. Preferred examples of such bleach activators include: (6-octanamidocaproyl) oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate and mixtures thereof.

Other useful activators, disclosed in U.S. 5,698,504, U.S. 5,695,679, U.S. 5,686,014 each of which is cited herein above and U.S. 4,966,723Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a C_6H_4 ring to which is fused in the 1,2-positions a moiety --$C(O)OC(R^1)$=N-.

Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

Transition Metal Bleach Catalyst

The laundry detergent compositions of the present invention optionally comprises a bleaching system which contains one or more bleach catalysts. Selected bleach catalysts *inter alia* 5,12-dimethyl-1,5,8,12-tertaaza-bicyclo[6.6.2]hexadecane manganese (II) chloride may be

formulated into bleaching systems which do not require a source of hydrogen peroxide or peroxygen bleach. The compositions comprise from about 1 ppb (0.0000001%), more preferably from about 100 ppb (0.00001%), yet more preferably from about 500 ppb (0.00005%), still more preferably from about 1 ppm (0.0001%) to about 99.9%, more preferably to about 50%, yet more preferably to about 5%, still more preferably to about 500 ppm (0.05%) by weight of the composition, of a transition-metal bleach catalyst

Non-limiting examples of suitable manganese-based catalysts are disclosed in U.S. 5,576,282 Miracle et al., issued November 19, 1996; U.S. 5,246,621 Favre et al., issued September 21, 1993; U.S. 5,244,594 Favre et al., issued September 14, 1993; U.S. 5,194,416 Jureller et al., issued March 16, 1993; U.S. 5,114,606 van Vliet et al., issued May 19, 1992; U.S. 4,430,243 Bragg, issued February 7, 1984; U.S. 5,114,611 van Kralingen, issued May 19, 1992; U.S. 4,728,455 Rerek, issued March 1, 1988; U.S. 5,284,944 Madison, issued February 8, 1994; U.S. 5,246,612 van Dijk et al., issued September 21, 1993; U.S. 5,256,779 Kerschner et al., issued October 26, 2993; U.S. 5,280,117 Kerschner et al., issued January 18, 1994; U.S. 5,274,147 Kerschner et al., issued December 28, 1993; U.S. 5,153,161 Kerschner et al., issued October 6, 1992; and U.S. 5,227,084 Martens et al., issued July 13, 1993; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1.

Non-limiting examples of suitable cobalt-based catalysts are disclosed in U.S. 5,597,936 Perkins et al., issued January 28, 1997; U.S. 5,595,967 Miracle et al., issued January 21, 1997; U.S. 5,703,030 Perkins et al., issued December 30, 1997; U.S. Patent 4,810,410 Diakun et al, issued March 7,1989; M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", *Adv. Inorg. Bioinorg. Mech.*, (1983), 2, pages 1-94; *J. Chem. Ed.* (1989), **66** (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. *Chem.*, **18**, 1497-1502 (1979); *Inorg. Chem.*, **21**, 2881-2885 (1982); *Inorg. Chem.*, **18**, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and *Journal of Physical Chemistry*, 56, 22-25 (1952).

Further examples of preferred macrocyclic ligand comprising bleach catalysts are described in WO 98/39406 A1 published September 11, 1998 and included herein by reference. Suitable examples of these bleach catalysts include:

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane manganese(II)

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane manganese(II) hexafluorophosphate

Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane manganese(III) hexafluorophosphate

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane manganese(II) tetrafluoroborate

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane manganese(III) hexafluorophosphate

Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza bicyclo[6.6.2]hexadecane manganese(II)

Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane manganese(II)

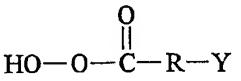
Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane manganese(II)

Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane manganese(II)

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane manganese(II).

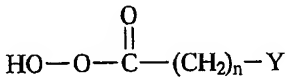
Pre-formed Bleaching Agents

The bleaching systems of the present invention may optionally further comprise from 0.1%, preferably from 1%, more preferably from 5% to about 10%, preferably to about 7% by weight, of one or more pre-formed bleaching agents. Pre-formed bleaching materials typically have the general formula:



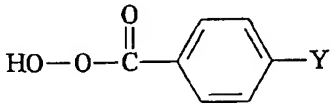
wherein R is a C_1-C_{22} alkylene, C_1-C_{22} substituted alkylene, phenylene, C_6-C_{22} substituted phenylene, and mixtures thereof, Y is hydrogen, halogen, alkyl, aryl, -C(O)OH, -C(O)OOH, and mixtures thereof.

The organic percarboxylic acids usable in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic percarboxylic acid is aliphatic, the unsubstituted acid has the general formula:



wherein Y can be hydrogen, methyl, methyl chloride, carboxylate, percarboxylate; and n is an integer having the value from 1 to 20.

When the organic percarboxylic acid is aromatic, the unsubstituted acid has the general formula:



wherein Y can be hydrogen, alkyl, haloalkyl, carboxylate, percarboxylate, and mixtures thereof.

Typical monoperoxy percarboxylic acids useful herein include alkyl percarboxylic acids and aryl percarboxylic acids such as:

i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy-o-naphthoic acid;

ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxylauric acid, peroxystearic acid, and N,N-phthaloylaminoperoxycaproic acid (PAP).

Typical diperoxy percarboxylic acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as:

iii) 1,12-diperoxydodecanedioic acid;

iv) 1,9-diperoxyazelaic acid;

v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

vi) 2-decyldiperoxybutane-1,4-dioic acid;

vii) 4,4'-sulfonybisperoxybenzoic acid.

A non-limiting example of a highly preferred pre-formed bleach includes 6-nonylamino-6-oxoperoxycaproic acid (NAPAA) as described in U.S. Pat. No. 4,634,551 Burns et al., issued Jan. 6, 1987 included herein by reference.

As well as the herein described peroxygen bleaching compositions, the compositions of the present invention may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC"). However, chlorine-type bleaches are less preferred for compositions which comprise enzymes.

ADJUNCT INGREDIENTS

The following are non-limiting examples of adjunct ingredients useful in the liquid laundry compositions of the present invention, said adjunct ingredients include enzymes, enzyme stabilizers, builders, optical brighteners, soil release polymers, dye transfer agents, dispersents, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

Enzymes

Enzymes are a preferred adjunct ingredient of the present invention. The selection of enzymes is left to the formulator, however, the examples herein below illustrate the use of enzymes in the liquid laundry detergents of the present invention.

"Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a liquid laundry, hard surface cleaning or personal care detergent composition. Preferred detersive enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for liquid laundry purposes include, but are not limited to, *inter alia* proteases, cellulases, lipases and peroxidases.

Protease Enzymes

The preferred liquid laundry detergent compositions according to the present invention further comprise at least 0.001% by weight, of a protease enzyme. However, an effective amount of protease enzyme is sufficient for use in the liquid laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. The protease enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Preferred liquid laundry detergent compositions of the present invention comprise modified protease enzymes derived from *Bacillus amyloliquefaciens* or *Bacillus lentus*. For the purposes of the present invention, protease enzymes derived from *B. amyloliquefaciens* are further referred to as "subtilisin BPN'" also referred to as "Protease A" and protease enzymes derived from *B. Lentus* are further referred to as "subtilisin 309". For the purposes of the present invention, the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, serves as the amino acid sequence numbering system for both subtilisin BPN' and subtilisin 309.

Derivatives of *Bacillus amyloliquefaciens* subtilisin -BPN' enzymes

A preferred protease enzyme for use in the present invention is a variant of Protease A (BPN') which is a non-naturally occurring carbonyl hydrolase variant having a different proteolytic activity, stability, substrate specificity, pH profile and/or performance characteristic as compared

to the precursor carbonyl hydrolase from which the amino acid sequence of the variant is derived. This variant of BPN' is disclosed in EP 130,756 A, January 9, 1985. Specifically Protease A-BSV is BPN' wherein the Gly at position 166 is replaced with Asn, Ser, Lys, Arg, His, Gln, Ala, or Glu; the Gly at position 169 is replaced with Ser; the Met at position 222 is replaced with Gln, Phe, Cys, His, Asn, Glu, Ala or Thr; or alternatively the Gly at position 166 is replaced with Lys, and the Met at position 222 is replaced with Cys; or alternatively the Gly at position 169 is replaced with Ala and the Met at position 222 is replaced with Ala.

Protease B

A preferred protease enzyme for use in the present invention is Protease B. Protease B is a non-naturally occurring carbonyl hydrolase variant having a different proteolytic activity, stability, substrate specificity, pH profile and/or performance characteristic as compared to the precursor carbonyl hydrolase from which the amino acid sequence of the variant is derived. Protease B is a variant of BPN' in which tyrosine is replaced with leucine at position +217 and as further disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985.

Bleach Stable Variants of Protease B (Protease B-BSV)

A preferred protease enzyme for use in the present invention are bleach stable variants of Protease B. Specifically Protease B-BSV are variants wherein the Gly at position 166 is replaced with Asn, Ser, Lys, Arg, His, Gln, Ala, or Glu; the Gly at position 169 is replaced with Ser; the Met at position 222 is replaced with Gln, Phe, Cys, His, Asn, Glu, Ala or Thr; or alternatively the Gly at position 166 is replaced with Lys, and the Met at position 222 is replaced with Cys; or alternatively the Gly at position 169 is replaced with Ala and the Met at position 222 is replaced with Ala.

Surface Active Variants of Protease B

Preferred Surface Active Variants of Protease B comprise BPN' wild-type amino acid sequence in which tyrosine is replaced with leucine at position +217, wherein the wild-type amino acid sequence at one or more of positions 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 218, 219 or 220 is substituted; wherein the BPN' variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin BPN'. Preferably, the positions having a substituted amino acid are 199, 200, 201, 202, 205, 207, 208, 209, 210, 211, 212, or 215; more preferably, 200, 201, 202, 205 or 207.

Also preferred proteases derived from *Bacillus amyloliquefaciens* subtilisin are subtilisin BPN' enzymes that have been modified by mutating the various nucleotide sequences that code for

the enzyme, thereby modifying the amino acid sequence of the enzyme. These modified subtilisin enzymes have decreased adsorption to and increased hydrolysis of an insoluble substrate as compared to the wild-type subtilisin. Also suitable are mutant genes encoding for such BPN' variants.

Derivatives of subtilisin 309

Further preferred protease enzymes for use according to the present invention also include the "subtilisin 309" variants. These protease enzymes include several classes of subtilisin 309 variants described herein below.

Protease C

A preferred protease enzyme for use in the compositions of the present invention Protease C. Protease C is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

Protease D

A preferred protease enzyme for use in the present invention is Protease D. Protease D is a carbonyl hydrolase variant derived from *Bacillus lentus* subtilisin having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

A. Loop Region 6 Substitution Variants - These subtilisin 309-type variants have a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more of positions 193, 194, 195, 196, 197, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213 or 214; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309. Preferably these proteases have

amino acids substituted at 193, 194, 195, 196, 199, 201, 202, 203, 204, 205, 206 or 209; more preferably 194, 195, 196, 199 or 200.

B. Multi-Loop Regions Substitution Variants - These subtilisin 309 variants may also be a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more positions in one or more of the first, second, third, fourth, or fifth loop regions; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309.

C. Substitutions at positions other than the loop regions - In addition, one or more substitution of wild-type subtilisin 309 may be made at positions other than positions in the loop regions, for example, at position 74. If the additional substitution to the subtilisin 309 is mad at position 74 alone, the substitution is preferably with Asn, Asp, Glu, Gly, His, Lys, Phe or Pro, preferably His or Asp. However modifications can be made to one or more loop positions as well as position 74, for example residues 97, 99, 101, 102, 105 and 121.

Subtilisin BPN' variants and subtilisin 309 variants are further described in WO 95/29979, WO 95/30010 and WO 95/30011, all of which were published November 9, 1995, all of which are incorporated herein by reference.

A further preferred protease enzyme for use in combination with the modified polyamines of the present invention is ALCALASE® from Novo. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble . When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Other particularly useful proteases are multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at an

amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT Application Nos. PCT/US98/22588, PCT/US98/22482 and PCT/US98/22486 all filed on October 23, 1998 from The Procter & Gamble Company (P&G Cases 7280&, 7281& and 7282L, respectively).

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Commercially available proteases useful in the present invention are known as ESPERASE®, ALCALASE®, DURAZYM®, SAVINASE®, EVERLASE® and KANNASE®

all from Novo Nordisk A/S of Denmark, and as MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® all from Genencor International (formerly Gist-Brocades of The Netherlands).

In addition to the above-described protease enzymes, other enzymes suitable for use in the liquid laundry detergent compositions of the present invention are further described herein below.

Other Enzymes

Enzymes in addition to the protease enzyme can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable enzymes include amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from about 0.001%, preferably from about 0.01% to about 5%, preferably to about 1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents, it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Amylases suitable herein include, for example, α-amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June

1985, pp 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide / tetraacetylethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Baccillus* amylases, especially the *Bacillus* α-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens, B. subtilis,* or *B. stearothermophilus;* (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those

described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139 McCarty et al., issued January 5, 1971. Enzymes

are further disclosed in U.S. 4,101,457 Place et al, issued July 18, 1978, and U.S. 4,507,219 Hughes, issued March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868 Hora et al., issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319 Gedge et al., issued August 17, 1971; EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

A further preferred enzyme according to the present invention are mannanase enzymes. When present mannanase enzymes comprise from about 0.0001%, preferably from 0.0005%, more preferably from about 0.001% to about 2%, preferably to about 0.1% more preferably to about 0.02% by weight, of said composition.

Preferably, the following three mannans-degrading enzymes : EC 3.2.1.25 : β-mannosidase, EC 3.2.1.78 : Endo-1,4-β-mannosidase, referred therein after as "mannanase" and EC 3.2.1.100 : 1,4-β-mannobiosidase (IUPAC Classification- Enzyme nomenclature, 1992 ISBN 0-12-227165-3 Academic Press) are useful in the compositions of the present invention.

More preferably, the detergent compositions of the present invention comprise a β-1,4-Mannosidase (E.C. 3.2.1.78) referred to as Mannanase. The term "mannanase" or "galactomannanase" denotes a mannanase enzyme defined according to the art as officially being named mannan endo-1,4-beta-mannosidase and having the alternative names beta-mannanase and endo-1,4-mannanase and catalysing the reaction: random hydrolysis of 1,4-beta-D- mannosidic linkages in mannans, galactomannans, glucomannans, and galactoglucomannans.

In particular, Mannanases (EC 3.2.1.78) constitute a group of polysaccharases which degrade mannans and denote enzymes which are capable of cleaving polyose chains containing mannose units, i.e. are capable of cleaving glycosidic bonds in mannans, glucomannans, galactomannans and galactogluco-mannans. Mannans are polysaccharides having a backbone composed of β-1,4- linked mannose; glucomannans are polysaccharides having a backbone or more or less regularly alternating β-1,4 linked mannose and glucose; galactomannans and galactoglucomannans are mannans and glucomannans with α-1,6 linked galactose sidebranches. These compounds may be acetylated.

The degradation of galactomannans and galactoglucomannans is facilitated by full or partial removal of the galactose sidebranches. Further the degradation of the acetylated mannans,

glucomannans, galactomannans and galactogluco-mannans is facilitated by full or partial deacetylation. Acetyl groups can be removed by alkali or by mannan acetylesterases. The oligomers which are released from the mannanases or by a combination of mannanases and α-galactosidase and/or mannan acetyl esterases can be further degraded to release free maltose by β-mannosidase and/or β-glucosidase.

Mannanases have been identified in several *Bacillus* organisms. For example, Talbot et al., *Appl. Environ. Microbiol.*, Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus* in dimer form having molecular weight of 162 kDa and an optimum pH of 5.5-7.5. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from *Bacillus subtilis* having a molecular weight of 38 kDa, an optimum activity at pH 5.0 and 55C and a pI of 4.8. JP-03047076 discloses a beta-mannanase derived from *Bacillus* sp., having a molecular weight of 373 kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. JP-63056289 describes the production of an alkaline, thermostable beta-mannanase which hydrolyses beta-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno-oligosaccharides. JP-63036774 relates to the *Bacillus* microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase at an alkaline pH. JP-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp. AM-001. A purified mannanase from *Bacillus amyloliquefaciens* useful in the bleaching of pulp and paper and a method of preparation thereof is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active at an extreme pH and temperature. WO 94/25576 discloses an enzyme from *Aspergillus aculeatus*, CBS 101.43, exhibiting mannanase activity which may be useful for degradation or modification of plant or algae cell wall material. WO 93/24622 discloses a mannanase isolated from *Trichoderma reseei* useful for bleaching lignocellulosic pulps. An hemicellulase capable of degrading mannan-containing hemicellulose is described in WO91/18974 and a purified mannanase from *Bacillus amyloliquefaciens* is described in WO97/11164.

Preferably, the mannanase enzyme will be an alkaline mannanase as defined below, more preferably, a mannanase originating from a bacterial source. Especially, the laundry detergent composition of the present invention will comprise an alkaline mannanase selected from the mannanase from the strain *Bacillus agaradherens* NICMB 40482; the mannanase from *Bacillus* strain 168, gene yght; the mannanase from *Bacillus sp.* I633 and/or the mannanase from *Bacillus sp.* AAI12. Most preferred mannanase for the inclusion in the detergent compositions of the present

invention is the mannanase enzyme originating from *Bacillus sp.* I633 as described in the co-pending application No. PA 1998 01340.

The terms "alkaline mannanase enzyme" is meant to encompass an enzyme having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a given pH ranging from 7 to 12, preferably 7.5 to 10.5.

The alkaline mannanase from *Bacillus agaradherens* NICMB 40482 is described in the co-pending U.S. patent application serial No. 09/111,256. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus agaradherens*, NCIMB 40482; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 32-343 of SEQ ID NO:2 as shown in U.S. patent application serial No. 09/111,256; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 97 to nucleotide 1029 as shown in U.S. patent application serial No. 09/111,256;

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 32 to amino acid residue 343 as shown in U.S. patent application serial No. 09/111,256;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pSJ1678 comprising the polynucleotide molecule (the DNA sequence) encoding said mannanase has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von

Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 18 May 1998 under the deposition number DSM 12180.

A second more preferred enzyme is the mannanase from the *Bacillus subtilis* strain 168, which is described in the co-pending U.S. patent application serial No. 09/095,163. More specifically, this mannanase is:

i) is encoded by the coding part of the DNA sequence shown in SED ID No. 5 shown in the U.S. patent application serial No. 09/095,163 or an analogue of said sequence; and/or

ii) a polypeptide comprising an amino acid sequence as shown SEQ ID NO:6 shown in the U.S. patent application serial No. 09/095,163; or

iii) an analogue of the polypeptide defined in ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed in the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO:5 as shown in the U.S. patent application serial No. 09/095,163

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 6 as shown in the U.S. patent application serial No. 09/095,163;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

A third more preferred mannanase is described in the co-pending Danish patent application No. PA 1998 01340. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* I633;

ii) a polypeptide comprising an amino acid sequence as shown in positions 33-340 of SEQ ID NO:2 as shown in the Danish application No. PA 1998 01340; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by

substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of:

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 317 to nucleotide 1243 the Danish application No. PA 1998 01340;

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 33 to amino acid residue 340 the Danish application No. PA 1998 01340;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM3 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 29 May 1998 under the deposition number DSM 12197.

A fourth more preferred mannanase is described in the Danish co-pending patent application No. PA 1998 01341. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* AAI 12;

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-362 of SEQ ID NO:2as shown in the Danish application No. PA 1998 01341; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 225 to nucleotide 1236 as shown in the Danish application No. PA 1998 01341;

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 25 to amino acid residue 362 as shown in the Danish application No. PA 1998 01341;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM1 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 7 October 1998 under the deposition number DSM 12433.

The compositions of the present invention may also comprise a xyloglucanase enzyme. Suitable xyloglucanases for the purpose of the present invention are enzymes exhibiting endoglucanase activity specific for xyloglucan. The xyloglucanase is incorporated into the compositions of the invention preferably at a level of from 0.0001%, more preferably from 0.0005%, most preferably from 0.001% to 2%, preferably to 0.1%, more preferably to 0.02% by weight, of pure enzyme.

As used herein, the term "endoglucanase activity" means the capability of the enzyme to hydrolyze 1,4-β-D-glycosidic linkages present in any cellulosic material, such as cellulose, cellulose derivatives, lichenin, β-D-glucan, or xyloglucan. The endoglucanase activity may be determined in accordance with methods known in the art, examples of which are described in WO 94/14953 and hereinafter. One unit of endoglucanase activity (e.g. CMCU, AVIU, XGU or BGU) is defined as the production of 1 μmol reducing sugar/min from a glucan substrate, the glucan substrate being, e.g., CMC (CMCU), acid swollen Avicell (AVIU), xyloglucan (XGU) or cereal β-

glucan (BGU). The reducing sugars are determined as described in WO 94/14953 and hereinafter. The specific activity of an endoglucanase towards a substrate is defined as units/mg of protein.

More specifically, as used herein the term "specific for xyloglucan" means that the endoglucanase enzyme exhibits its highest endoglucanase activity on a xyloglucan substrate, and preferably less than 75% activity, more preferably less than 50% activity, most preferably less than about 25% activity, on other cellulose-containing substrates such as carboxymethyl cellulose, cellulose, or other glucans.

Preferably, the specificity of an endoglucanase towards xyloglucan is further defined as a relative activity determined as the release of reducing sugars at optimal conditions obtained by incubation of the enzyme with xyloglucan and the other substrate to be tested, respectively. For instance, the specificity may be defined as the xyloglucan to β-glucan activity (XGU/BGU), xyloglucan to carboxy methyl cellulose activity (XGU/CMCU), or xyloglucan to acid swollen Avicell activity (XGU/AVIU), which is preferably greater than about 50, such as 75, 90 or 100.

The term "derived from" as used herein refers not only to an endoglucanase produced by strain CBS 101.43, but also an endoglucanase encoded by a DNA sequence isolated from strain CBS 101.43 and produced in a host organism transformed with said DNA sequence. The term "homologue" as used herein indicates a polypeptide encoded by DNA which hybridizes to the same probe as the DNA coding for an endoglucanase enzyme specific for xyloglucan under certain specified conditions (such as presoaking in 5xSSC and pre-hybridizing for 1 h at -40°C in a solution of 5xSSC, 5xDenhardt's solution, and 50 μg of denatured sonicated calf thymus DNA, followed by hybridization in the same solution supplemented with 50 μCi 32-P-dCTP labeled probe for 18 h at -40°C and washing three times in 2xSSC, 0.2% SDS at 40°C for 30 minutes). More specifically, the term is intended to refer to a DNA sequence which is at least 70% homologous to any of the sequences shown above encoding an endoglucanase specific for xyloglucan, including at least 75%, at least 80%, at least 85%, at least 90% or even at least 95% with any of the sequences shown above. The term is intended to include modifications of any of the DNA sequences shown above, such as nucleotide substitutions which do not give rise to another amino acid sequence of the polypeptide encoded by the sequence, but which correspond to the codon usage of the host organism into which a DNA construct comprising any of the DNA sequences is introduced or nucleotide substitutions which do give rise to a different amino acid sequence and therefore, possibly, a different amino acid sequence and therefore, possibly, a different protein structure which might give rise to an endoglucanase mutant with different properties than the native enzyme.

Other examples of possible modifications are insertion of one or more nucleotides into the sequence, addition of one or more nucleotides at either end of the sequence, or deletion of one or more nucleotides at either end or within the sequence.

Endoglucanase specific for xyloglucan useful in the present invention preferably is one which has a XGU/BGU, XGU/CMU and/or XGU/AVIU ratio (as defined above) of more than 50, such as 75, 90 or 100.

Furthermore, the endoglucanase specific for xyloglucan is preferably substantially devoid of activity towards β-glucan and/or exhibits at the most 25% such as at the most 10% or about 5%, activity towards carboxymethyl cellulose and/or Avicell when the activity towards xyloglucan is 100%. In addition, endoglucanase specific for xyloglucan of the invention is preferably substantially devoid of transferase activity, an activity which has been observed for most endoglucanases specific for xyloglucan of plant origin.

Endoglucanase specific for xyloglucan may be obtained from the fungal species *A. aculeatus*, as described in WO 94/14953. Microbial endoglucanases specific for xyloglucan has also been described in WO 94/14953. Endoglucanases specific for xyloglucan from plants have been described, but these enzymes have transferase activity and therefore must be considered inferior to microbial endoglucanases specific for xyloglucan whenever extensive degradation of xyloglucan is desirable. An additional advantage of a microbial enzyme is that it, in general, may be produced in higher amounts in a microbial host, than enzymes of other origins.

Enzyme Stabilizing System

Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001%, preferably from about 0.005%, more preferably from about 0.01% to about 10%, preferably to about 8%, more preferably to about 6% by weight, of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is

being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species disclosed in U.S. 4,537,706 Severson, issued August 27, 1985. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions may further comprise from 0, preferably from about 0.01% to about 10%, preferably to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special

enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392 Baginski et al., issued March 24, 1987.

Builders

The laundry detergent compositions of the present invention preferably comprise one or more detergent builders or builder systems. When present, the compositions will typically comprise at least about 1% builder, preferably from about 5%, more preferably from about 10% to about 80%, preferably to about 50%, more preferably to about 30% by weight, of detergent builder.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and

aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. 4,664,839 Rieck, issued May 12, 1987. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1} \cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$[M_z(zAlO_2)_y].xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669, Krummel et al, issued October 12, 1976. Preferred

synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "poly-carboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in U.S. 3,128,287 Berg, issued April 7, 1964, and U.S. 3,635,830 Lamberti et al., issued January 18, 1972. See also "TMS/TDS" builders of U.S. 4,663,071 Bush et al., issued May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679 Rapko, issued December 2, 1975; U.S. 4,158,635 Crutchfield et al., issued June 19, 1979; U.S. 4,120,874 Crutchfield et al., issued October 17, 1978; and U.S. 4,102,903 Crutchfield et al., issued July 25, 1978.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used

in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al., issued March 13, 1979 and in U.S. 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Dispersants

A description of other suitable polyalkyleneimine dispersants which may be optionally combined with the bleach stable dispersants of the present invention can be found in U.S. 4,597,898 Vander Meer, issued July 1, 1986; European Patent Application 111,965 Oh and Gosselink, published June 27, 1984; European Patent Application 111,984 Gosselink, published June 27, 1984; European Patent Application 112,592 Gosselink, published July 4, 1984; U.S. 4,548,744 Connor, issued October 22, 1985; and U.S. 5,565,145 Watson et al., issued October 15, 1996; all of which are included herein by reference. However, any suitable clay/soil dispersant or anti-redepostion agent can be used in the laundry compositions of the present invention.

In addition, polymeric dispersing agents which include polymeric polycarboxylates and polyethylene glycols, are suitable for use in the present invention. Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in U.S. 3,308,067 Diehl, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000, preferably from about 5,000, more preferably from about 7,000 to 100,000, more preferably to 75,000, most preferably to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Soil Release Agents

The compositions according to the present invention may optionally comprise one or more soil release agents. If utilized, soil release agents will generally comprise from about 0.01%, preferably from about 0.1%, more preferably from about 0.2% to about 10%, preferably to about 5%, more preferably to about 3% by weight, of the composition. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of the laundry cycle and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occuring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

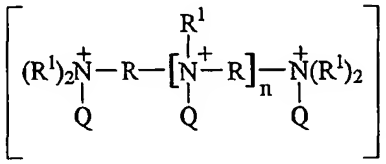
The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 5,843,878 Gosselink et al., issued December 1, 1998; U.S. 5,834,412 Rohrbaugh *et al.*, issued November 10, 1998; U.S. 5,728,671 Rohrbaugh *et al.*, issued March 17, 1998; U.S. 5,691,298 Gosselink *et al.*, issued November 25, 1997; U.S. 5,599,782 Pan *et al.*, issued February 4, 1997; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; U.S. 5,182,043 Morrall *et al.*, issued January 26, 1993; U.S. 4,956,447 Gosselink *et al.*, issued September 11, 1990; U.S. 4,976,879 Maldonado *et al.* issued December 11, 1990; U.S. 4,968,451 Scheibel *et al.*, issued November 6, 1990; U.S. 4,925,577 Borcher, Sr. *et al.*, issued May 15, 1990; U.S. 4,861,512 Gosselink, issued August 29, 1989; U.S. 4,877,896 Maldonado *et al.*, issued October 31, 1989; U.S. 4,771,730 Gosselink *et al.*, issued October 27, 1987; U.S. 711,730 Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580 Gosselink issued January 26, 1988; U.S. 4,000,093 Nicol *et al.*, issued December 28, 1976; U.S. 3,959,230 Hayes, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; and European Patent Application 0 219 048, published April 22, 1987 by Kud *et al.*

Further suitable soil release agents are described in U.S. 4,201,824 Voilland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681 Ruppert *et al.*; U.S. 4,220,918; U.S. 4,787,989; EP 279,134 A, 1988 to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N.V., 1974; all incorporated herein by reference.

METHOD OF USE

The present invention further relates to a method for removing hydrophobic soils, *inter alia*, body oils, perspiration and other human body soils form fabric, preferably clothing, said method comprising the step of contacting fabric in need of cleaning with an aqueous solution containing at least 0.01% by weight, of a laundry detergent composition comprising:

A) from about 0.01% by weight of a hydrophobically modified polyamine having the formula:



wherein R is C_5-C_{20} linear or branched alkylene, and mixtures thereof; R^1 is an alkyleneoxy unit having the formula:

$$-(R^2O)_x-R^3$$

wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^3 is an anionic unit, and mixtures thereof; x is from about 15 to about 30; Q is a hydrophobic quaternizing unit selected from the group consisting of C_8-C_{30} linear or branched alkyl, C_6-C_{30} cycloalkyl, C_7-C_{30} substituted or unsubstituted alkylenearyl, and mixtures thereof; X is an anion present in sufficient amount to provide electronic neutrality; n is from 0 to 4;

B) from about 0.01% by weight, of a surfactant system comprising one or more surfactants selected from:

i) from about 85%, preferably from about 90%, more preferably from about 95% by weight to about 99.9% by weight, of the surfactant system one or more nonionic surfactants;

ii) optionally and preferably, from 0.1%, preferably from about 5% more preferably from about 10% to about 15% by weight, of the surfactant system of one or more anionic surfactants;

iii) optionally and preferably, from 0.1%, preferably from about 5% more preferably from about 10% to about 15% by weight, of one or more zwitterionic, cationic, ampholytic surfactants, and mixtures thereof;

C) the balance carriers and adjunct ingredients

Preferably the aqueous solution comprises at least about 0.01% (100 ppm), preferably at least about 1% (1000 ppm)by weight, of said laundry detergent composition.

The compositions of the present invention can be suitably prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. 5,691,297 Nassano *et al.*, issued November 11, 1997; U.S. 5,574,005 Welch *et al.*, issued November 12, 1996; U.S. 5,569,645 Dinniwell *et al.*, issued October 29, 1996; U.S. 5,565,422 Del Greco *et al.*, issued October 15, 1996; U.S. 5,516,448 Capeci *et al.*, issued May 14, 1996; U.S. 5,489,392 Capeci *et al.*, issued February 6, 1996; U.S. 5,486,303 Capeci *et al.*, issued January 23, 1996 all of which are incorporated herein by reference.

EXAMPLE 1

Synthesis of ethoxylated (E20) bis(hexamethylene)triamine tribenzyl quaternary ammonium bromide

Ethoxylation of Bis(hexamethylene)triamine to Average E20 per NH - The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 362 g portion of Bis(hexamethylene)triamine (BHMT) (m.w. 215, (Aldrich), 1.68 moles, 5.04 moles nitrogen, 8.4 moles ethoxylatable (NH) sites, is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 80 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit

any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 370 grams of ethylene oxide (8.4 moles) has been charged to the autoclave, the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional 2 hours. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 181.5 g of a 25% sodium methoxide in methanol solution (0.84 moles, to achieve a 10% catalyst loading based upon ethoxylatable sites functions). The methoxide solution is removed from the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 100 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1.5 hours indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4180 g of ethylene oxide (95 mol, resulting in a total of 20 moles of ethylene oxide per mole of ethoxylatable sites on BHMT), the temperature is increased to 110 °C and the mixture stirred for an additional 2 hours.

The reaction mixture is then collected into a 22 L three neck round bottomed flask purged with nitrogen. The strong alkali catalyst is neutralized by slow addition of 80.7 g methanesulfonic acid (0.84 moles) with heating (100 °C) and mechanical stirring. The reaction mixture is then removed of residual ethylene oxide and deodorized by sparging an inert gas (argon or nitrogen) into the mixture through a gas dispersion frit while agitating and heating the mixture to 120 °C for 1 hour. The final reaction product is cooled slightly and stored in a glass container purged with nitrogen.

Quaternization of BHMT E20 to 90 mol% (3 mol N per mol polymer) - Into a weighed, 1000ml, 3 neck round bottom flask fitted with argon inlet, condenser, addition funnel, thermometer, mechanical stirring and argon outlet (connected to a bubbler) is added BHMT EO20 (522.8g, 0.333 mol N, 98% active, m.w.-4615) under argon. The material is heated to 80°C with stirring until melted. Next, benzyl bromide (61.6g, 0.36mol, Aldrich, m.w.-171.04) is slowly added to the melted BHMT EO20 using an addition funnel over a period of 10 minutes. The reaction complete after stirring at 80°C for 6 hours. The reaction mixture is dissolved in 500g water and adjusted to pH>7 using 1N NaOH followed by transfer to a plastic container for storage.

Sulfation of BHMT E20 to 90% - Under argon, the reaction mixture from the quaternization step is cooled to 5°C using an ice bath (BHMT E20, 90+mol% quat, 0.59 mol OH). Chlorosulfonic acid (72g, 0.61 mol, 99%, mw-116.52) is slowly added using an addition funnel. The temperature of the reaction mixture is not allowed to rise above 10°C. The ice bath is removed and the reaction is allowed to rise to room temperature. After 6 hrs. the reaction is complete. The reaction is again cooled to 5°C and sodium methoxide (264g, 1.22 mol, Aldrich, 25% in methanol, m.w.-54.02) is slowly added to the rapidly stirred mixture. The temperature of the reaction mixture is not allowed to rise above 10°C. The reaction mixture is transferred to a single neck round bottom flask. Purified water (1300ml) is added to the reaction mixture and the methylene chloride, methanol and some water is stripped off on a rotary evaporator at 50°C. The clear, light yellow solution is transferred to a bottle for storage. The final product pH is checked and adjusted to ~9 using 1N NaOH or 1N HCl as needed.

EXAMPLE 2

Synthesis of bis(hexamethylene)triamine, ethoxylate (E20), sulfated to approximately 40%, methyl quaternary ammonium bromide

Ethoxylation of Bis(hexamethylene)triamine to Average E20 per NH - The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 362 g portion of Bis(hexamethylene)triamine (BHMT) (m.w. 215, (Aldrich), 1.68 moles, 5.04 moles nitrogen, 8.4 moles ethoxylatable (NH) sites, is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 80 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 370 grams of ethylene oxide (8.4 moles) has been charged to the autoclave, the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional 2 hours. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 181.5 g of a 25% sodium methoxide in methanol solution (0.84 moles, to achieve a 10% catalyst loading based upon ethoxylatable sites functions). The methoxide solution is removed from the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 100 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1.5 hours indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4180 g of ethylene oxide (95 mol, resulting in a total of 20 moles of ethylene oxide per mole of ethoxylatable sites on BHMT), the temperature is increased to 110 °C and the mixture stirred for an additional 2 hours.

The reaction mixture is then collected into a 22 L three neck round bottomed flask purged with nitrogen. The strong alkali catalyst is neutralized by slow addition of 80.7 g methanesulfonic acid (0.84 moles) with heating (100 °C) and mechanical stirring. The reaction mixture is then removed of residual ethylene oxide and deodorized by sparging an inert gas (argon or nitrogen) into the mixture through a gas dispersion frit while agitating and heating the mixture to 120 °C for 1 hour. The final reaction product is cooled slightly and stored in a glass container purged with nitrogen.

Quaternization of BHMT E20 to 90 mol% (3 mol N per mol polymer) - Into a weighed, 1000ml, 3 neck round bottom flask fitted with argon inlet, condenser, addition funnel, thermometer, mechanical stirring and argon outlet (connected to a bubbler) is added BHMT EO20 (522.8g, 0.333 mol N, 98% active, m.w.-4615) under argon. The material is heated to 80°C with stirring until melted. Next, benzyl bromide (61.6g, 0.36mol, Aldrich, m.w.-171.04) is slowly added to the melted BHMT EO20 using an addition funnel over a period of 10 minutes. The reaction complete after stirring at 80°C for 6 hours. The reaction mixture is dissolved in 500g water and adjusted to pH>7 using 1N NaOH followed by transfer to a plastic container for storage.

Sulfation of BHMT E20 to 90% - Under argon, the reaction mixture from the quaternization step is cooled to 5°C using an ice bath (BHMT E20, 90+mol% quat, 0.59 mol OH). Chlorosulfonic acid (72g, 0.61 mol, 99%, mw-116.52) is slowly added using an addition funnel. The temperature of the reaction mixture is not allowed to rise above 10°C. The ice bath is removed and the reaction is allowed to rise to room temperature. After 6 hrs. the reaction is complete. The reaction is again cooled to 5°C and sodium methoxide (264g, 1.22 mol, Aldrich, 25% in methanol, m.w.-54.02) is slowly added to the rapidly stirred mixture. The temperature of the reaction mixture is not allowed to rise above 10°C. The reaction mixture is transferred to a single neck round bottom flask. Purified water (1300ml) is added to the reaction mixture and the methylene chloride, methanol and some water is stripped off on a rotary evaporator at 50°C. The clear, light yellow solution is transferred to a bottle for storage. The final product pH is checked and adjusted to ~9 using 1N NaOH or 1N HCl as needed.

The following are non-limiting examples of the compositions according to the present invention.

TABLE I

weight %

Ingredients	2	3	4	5
C_{14}-C_{15} alkyl E1.0 sulfate	22.5	22.5	22.5	22.5
Linear alkyl benzene sulfonate	3.0	3.0	3.0	3.0
C_{10} amidopropyl DMA	1.5	1.5	1.5	1.5
C_{12}-C_{14} alkyl E7.0	3.0	3.0	3.0	3.0
Citric Acid	2.5	2.5	2.5	2.5
C_{12}-C_{18} alkyl fatty acid	3.5	3.5	3.5	3.5
Rapeseed fatty acid	5.0	5.0	5.0	5.0
protease	0.8	1.57	1.57	1.57
amylase	0.055	0.088	0.088	0.088
cellulase	0.188	0.055	0.055	0.055
lipolase	0.06	--	--	--
mannanase	0.007	0.0033	0.0033	0.0033
Sodium metaborate	2.0	2.5	2.5	2.5
Ca formate/$CaCl_2$	0.02	0.10	0.10	0.10
Modified polyamine [1]				
Bleach catalyst [2]	0.035	0.034	0.034	0.034
Hydrophobic dispersant [3]	0.65	0.76	0.76	0.76
Soil release agent [4]	0.147	--	--	--
Soil release agent [5]	--	0.10	0.10	0.10
Suds suppresser	0.60	0.60	0.60	0.60
Water and minors	balance	balance	balance	balance

1. Hydrophobically modified polyamine according to Example 1.
2. 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonan-9-ol manganese(II) dichloride $1/2H_2O$.
3. PEI 189 E15-18 according to U.S. Patent 4,597,898 Vander Meer, issued July 1, 1986.
4. Soil release agent according to U.S. Patent 4,702,857 Gosselink, issued October 27, 1987.
5. Soil release agent according to U.S. Patent 4,968,451, Scheibel *et al.*, issued November 6, 1990.

The following examples include compositions which comprise an adjunct bleaching agent.

TABLE II

weight %

Ingredients	6	7	8	9
Sodium C_{11}-C_{13} alkylbenzene-sulfonate	13.3	13.7	10.4	11.1
Sodium C_{14}-C_{15} alcohol sulfate	3.9	4.0	4.5	11.2
Sodium C_{14}-C_{15} alcohol ethoxylate (0.5) sulfate	2.0	2.0	--	--
Sodium C_{14}-C_{15} alcohol ethoxylate (6.5)	0.5	0.5	0.5	1.0
Tallow fatty acid	--	--	--	1.1
Sodium tripolyphosphate	--	41.0	--	--
Zeolite A, hydrate (0.1-10 micron size)	26.3	--	21.3	28.0
Sodium carbonate	23.9	12.4	25.2	16.1
Sodium Polyacrylate (45%)	3.4	--	2.7	3.4
Sodium silicate (1:6 ratio NaO/SiO_2)(46%)	2.4	6.4	2.1	2.6
Sodium sulfate	10.5	10.9	8.2	15.0
Sodium perborate	1.0	1.0	5.0	--
Poly(ethyleneglycol), MW ~4000 (50%)	1.7	0.4	1.0	1.1
Citric acid	--	--	3.0	--
Bleach catalyst [1]	0.035	0.030	0.034	0.028
Bleach activator [2]	--	--	5.9	--
Soil release agent [3]	--	0.10	0.10	0.10
Polyamine [4]				
Suds suppresser	0.60	0.60	0.60	0.60
Water and minors [5]	balance	balance	balance	balance

1. 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonan-9-ol manganese(II) dichloride $1/2H_2O$.
2. Nonyl ester of sodium p-hydroxybenzene-sulfonate.
3. Soil release agent according to U.S. 5,415,807 Gosselink et al., issued May 16, 1995.
4. Hydrophobically modified polyamine according to Example 1.

5. Balance to 100% can, for example, include minors like optical brightener, perfume, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including $CaCO_3$, talc, silicates, etc.

The following is a non-limiting example of the bleaching system of the present invention in the absence of a source of hydrogen peroxide.

TABLE III

weight %

Ingredients	10	11	12	13
Sodium C_{11}-C_{13} alkylbenzene-sulfonate	13.3	13.7	10.4	11.1
Sodium C_{14}-C_{15} alcohol sulfate	3.9	4.0	4.5	11.2
Sodium C_{14}-C_{15} alcohol ethoxylate (0.5) sulfate	2.0	2.0	--	--
Sodium C_{14}-C_{15} alcohol ethoxylate (6.5)	0.5	0.5	0.5	1.0
Tallow fatty acid	--	--	--	1.1
Sodium tripolyphosphate	--	41.0	--	--
Zeolite A, hydrate (0.1-10 micron size)	26.3	--	21.3	28.0
Sodium carbonate	23.9	12.4	25.2	16.1
Sodium Polyacrylate (45%)	3.4	--	2.7	3.4
Sodium silicate (1:6 ratio NaO/SiO_2)(46%)	2.4	6.4	2.1	2.6
Sodium sulfate	10.5	10.9	8.2	15.0
Poly(ethyleneglycol), MW ~4000 (50%)	1.7	0.4	1.0	1.1
Citric acid	--	--	3.0	--
Bleach catalyst [1]	0.10	0.07	0.035	0.028
Hydrophobically modified polyamine [2]				
Hydrophobic dispersant [5]	0.65	0.76	0.76	0.76
Soil release agent [6]	0.147	0.10	0.10	0.10
Suds suppresser	0.60	0.60	0.60	0.60
Water and minors [7]	balance	balance	balance	balance

1. 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonan-9-ol manganese(II) dichloride $1/2H_2O$.
2. Hydrophobically modified polyamine according to Example 1.

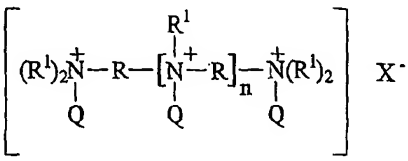
3. Potassium sulfite.
4. PEI 189 E15-18 according to U.S. Patent 4,597,898 Vander Meer, issued July 1, 1986.
6. Soil release agent according to U.S. 5,415,807 Gosselink et al., issued May 16, 1995.
7. Balance to 100% can, for example, include minors like optical brightener, perfume, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including $CaCO_3$, talc, silicates, etc.

The compositions of the present invention can be suitably prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. 5,691,297 Nassano et al., issued November 11, 1997; U.S. 5,574,005 Welch et al., issued November 12, 1996; U.S. 5,569,645 Dinniwell et al., issued October 29, 1996; U.S. 5,565,422 Del Greco et al., issued October 15, 1996; U.S. 5,516,448 Capeci et al., issued May 14, 1996; U.S. 5,489,392 Capeci et al., issued February 6, 1996; U.S. 5,486,303 Capeci et al., issued January 23, 1996 all of which are incorporated herein by reference.

WHAT IS CLAIMED IS:

1. A laundry detergent composition comprising:

A) from 0.01% by weight, of a hydrophobically modified polyamine having the formula:



wherein R is C_5-C_{20} linear or branched alkylene, and mixtures thereof; R^1 is an alkyleneoxy unit having the formula:

$$-(R^2O)_x-R^3$$

wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^3 an anionic unit, and mixtures thereof; x is from 15 to 30; Q is a hydrophobic quaternizing unit selected from the group consisting of C_8-C_{30} linear or branched alkyl, C_6-C_{30} cycloalkyl, C_7-C_{30} substituted or unsubstituted alkylenearyl, and mixtures thereof; X is an anion present in sufficient amount to provide electronic neutrality; n is from 0 to 4;

B) from 0.01% by weight, of a surfactant system comprising one or more nonionic surfactants; and

C) the balance carriers and adjunct ingredients

2. A composition according to Claim 1 wherein R is C_6-C_{10} alkylene, and mixtures thereof.

3. A composition according to Claim 2 wherein R is hexylene.

4. A composition according to Claim 1 wherein R^2 is ethylene, 1,2-propylene, and mixtures thereof.

5. A composition according to Claim 4 wherein R^2 is ethylene.

6. A composition according to Claim 4 wherein R^3 is selected from the group consisting of:

a) $-(CH_2)_fCO_2M$;

b) $-C(O)(CH_2)_fCO_2M$;

c) $-(CH_2)_fPO_3M$;

d) $-(CH_2)_fOPO_3M$;

e) $-(CH_2)_fSO_3M$;

f) $-CH_2(CHSO_3M)(CH_2)_fSO_3M$;

g) $-CH_2(CHSO_2M)(CH_2)_fSO_3M$;

h) $-C(O)CH_2CH(SO_3M)CO_2M$;

i) $-C(O)CH_2CH(CO_2M)NHCH(CO_2M)CH_2CO_2M$;

j) and mixtures thereof;

wherein M is hydrogen or a cation which provides charge neutrality.

7. A composition according to Claim 4 wherein the index x is from 15 to 25.

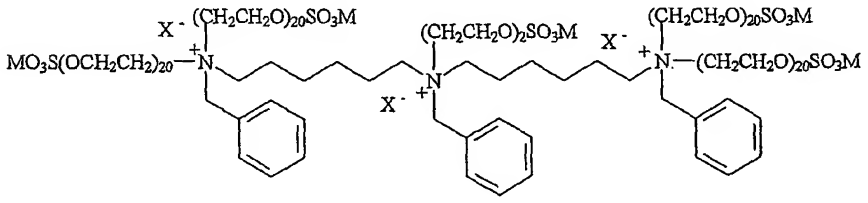
8. A composition according to Claim 7 wherein the index x is 20.

9. A composition according to Claim 1 wherein Q is C_{12}-C_{18} linear alkyl, C_7-C_{12} substituted or unsubstituted alkylenearyl, and mixtures thereof.

10. A composition according to Claim 9 wherein Q is benzyl.

11. A composition according to Claim 1 wherein the index n is 0 or 1.

12. A composition according to Claim 1 wherein said hydrophobically modified polyamine has the formula:



wherein X is a water soluble anion selected from the group consisting of chlorine, bromine, iodine, methylsulfate, and mixtures thereof.

13. A composition according to Claim 1 wherein said surfactant system comprises from 0.01% by weight, of one or more surfactants selected from:

i) from 85% to 99.9% by weight, of one or more nonionic surfactants;

ii) optionally, from 0.1% to 15% by weight, of one or more anionic surfactants;

iii) optionally from 0.1% to 15% by weight, of one or more cationic surfactants;

iv) optionally from 0.1% to 15% by weight, of one or more zwitterionic surfactants;

v) optionally from 0.1% to 15% by weight, of one or more ampholytic surfactants; or

vi) mixtures thereof.

14. A composition according to Claim 1 further comprising 1% by weight of a builder.

15. A composition according to Claim 1 further comprising from 1% by weight, of a peroxygen bleaching system comprising:

i) from 40% by weight, of the bleaching system, a source of hydrogen peroxide;

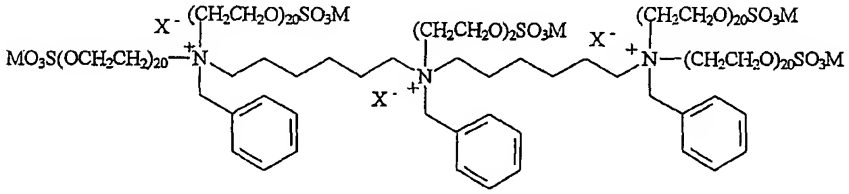
ii) optionally from 0.1% by weight, of the beaching system, a beach activator;

iii) optionally from 1 ppb of the composition, of a transition-metal bleach catalyst; and

iv) optionally from 0.1% by weight, of a pre-formed peroxygen bleaching agent.

16. A laundry detergent composition comprising:

A) from 0.01% by weight of a hydrophobically modified polyamine having the formula:



wherein M is a water soluble cation; X is a water soluble anion selected from the group consisting of chlorine, bromine, iodine, methylsulfate, and mixtures thereof

B) from 0.01% by weight, of a surfactant system comprising one or more surfactants selected from:

i) from 85% to 99.9% by weight, of one or more nonionic surfactants;

ii) optionally, from 0.1% to 15% by weight, of one or more anionic surfactants;

iii) optionally from 0.1% to 15% by weight, of one or more cationic surfactants;

iv) optionally from 0.1% to 15% by weight, of one or more zwitterionic surfactants;

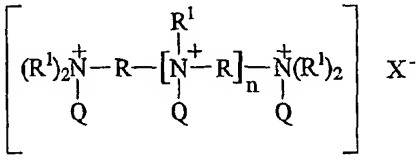
v) optionally from 0.1% to 15% by weight, of one or more ampholytic surfactants; or

vi) mixtures thereof;

C) the balance carriers and adjunct ingredients.

17. A method for cleaning fabric comprising the step of contacting an article of fabric with an aqueous solution containing at least 0.1% by weight of a composition comprising:

A) from 0.01% by weight of a hydrophobically modified polyamine having the formula:



wherein R is C_5-C_{20} linear or branched alkylene, and mixtures thereof; R^1 is an alkyleneoxy unit having the formula:

$$-(R^2O)_x-R^3$$

wherein R^2 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^3 is an anionic unit selected from the group consisting of:

a) $-(CH_2)_fCO_2M$;

b) $-C(O)(CH_2)_fCO_2M$;

c) $-(CH_2)_fPO_3M$;

d) $-(CH_2)_fOPO_3M$;

e) $-(CH_2)_fSO_3M$;

f) $-CH_2(CHSO_3M)(CH_2)_fSO_3M$;

g) $-CH_2(CHSO_2M)(CH_2)_fSO_3M$;

h) $-C(O)CH_2CH(SO_3M)CO_2M$;

i) $-C(O)CH_2CH(CO_2M)NHCH(CO_2M)CH_2CO_2M$;

j) and mixtures thereof;

wherein the index f is from 0 to 10; M is hydrogen or a cation which provides charge neutrality.; x is from 15 to 30; Q is a hydrophobic quaternizing unit selected from the group consisting of C_8-C_{30} linear or branched alkyl, C_6-C_{30} cycloalkyl, C_7-C_{30} substituted or unsubstituted alkylenearyl, and mixtures thereof; X is an anion present in sufficient amount to provide electronic neutrality; n is from 0 to 4;

B) from 0.01% by weight, of a surfactant system comprising one or more surfactants selected from:

i) from 85% to 99.9% by weight, of one or more nonionic surfactants;

ii) optionally, from 0.1% to 15% by weight, of one or more anionic surfactants;

iii) optionally from 0.1% to 15% by weight, of one or more cationic surfactants;

iv) optionally from 0.1% to 15% by weight, of one or more zwitterionic surfactants;

v) optionally from 0.1% to 15% by weight, of one or more ampholytic surfactants; or

vi) mixtures thereof

C) the balance carriers and adjunct ingredients.